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Published in:
Europhysics Letters

DOI:
[10.1209/epl/i1996-00543-x](https://doi.org/10.1209/epl/i1996-00543-x)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1996

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Lee, S. H., Broholm, C. L., Aeppli, G., Ramirez, A. P., Perring, T. G., Carlile, C. J., ... Hessen, B. (1996). Spin-glass and non-spin-glass features of a geometrically frustrated magnet. *Europhysics Letters*, 35(2), 127 - 132. <https://doi.org/10.1209/epl/i1996-00543-x>

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Spin-glass and non-spin-glass features of a geometrically frustrated magnet

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(received 9 February 1996; accepted in final form 24 May 1996)

PACS. 75.40Gb – Dynamic properties (dynamic susceptibility, spin waves, spin diffusion, dynamic scaling, etc.).

PACS. 75.25+z – Spin arrangements in magnetically ordered materials (including neutron and spin-polarized electron studies, synchrotron-source X-ray scattering, etc.).

PACS. 75.50Lk – Spin glasses and other random magnets.

Abstract. – We use neutron scattering to show that the low-temperature, short-range ordered spin configuration in the geometrically frustrated magnet $\text{SrCr}_{9p}\text{Ga}_{12-9p}\text{O}_{19}$ ($p = 0.92(5)$) is composed of small groups of spins whose dipole moments cancel. The local magnetic fluctuation spectrum, $\chi''(\omega)$, vanishes approximately in proportion to ω for $\hbar\omega < 0.5$ meV, distinguishing this magnet from conventional spin glasses which display a featureless continuum of excited states. We argue that this behavior results from the absence of local, low-energy excitations in the zero-spin clusters from which the frozen spin configuration is composed.

Frustration is an important concept because of the ubiquity of situations where several coupled degrees of freedom cannot simultaneously satisfy all mutual constraints. Perhaps the simplest realization of frustration is a triangle of spins A , B , C with equal and antiferromagnetic pairwise exchange couplings. If spins A and B are aligned in opposite directions to minimize the energy of the bond between them, spin C will be frustrated in the sense that it cannot minimize its interaction energies with A and B by being simultaneously antiparallel to A and B . When spins A , B , and C are simple Ising variables, the related ground-state degeneracy is high. For quantum or continuous classical spin degrees of freedom, however, frustration is relieved and the ground-state degeneracy reduced. While it is easy to find exact ground states

for small frustrated spin clusters, even today it is difficult to predict what will happen when many such clusters are attached to each other to form an infinite lattice [1], [2]. Experiment therefore retains a crucial role in revealing the possible ground states and excitations for such lattices. Of particular interest is whether there is any fundamental difference between conventional magnets with no frustration, structurally ordered but frustrated magnets, and magnets, often called spin glasses, whose frustration is derived from bond disorder. Magnets of the second type, which are also called geometrically frustrated magnets, can display quite conventional Néel order as for the triangular XY antiferromagnet. The purpose of the present paper is to show that this is not always the case. Specifically, we show that the geometrically frustrated magnet $\text{SrCr}_{9p}\text{Ga}_{12-9p}\text{O}_{19}$ (SCGO(p)) has spin correlations and fluctuations which distinguish it from both conventional spin glasses and antiferromagnets.

SCGO(p) is a two-dimensional magnet of antiferromagnetically interacting Cr^{3+} ions on the vertices of corner-sharing tetrahedra which form two kagomé lattices separated by a triangular lattice [3]-[9]. A kagomé lattice is a triangular lattice where 1/4 of the vertices have been removed to form an ordered triangular super-lattice of vacancies. The triangular motif and low connectivity of the kagomé lattice disfavor conventional long-range ordered antiferromagnetism [1], [2]. To examine spin correlations in SCGO(p) we measured the wave vector(Q)- and energy($\hbar\omega$)-dependent scattering function $S(Q, \omega)$, which is the Fourier transform of the distance and time-dependent two-spin correlation function. The key results are that despite the very short two-spin correlation length in SCGO(p), the material displays the following behavior which is usually associated with two-dimensional long-range ordered antiferromagnets: 1) at low T , $S(Q, \omega = 0)$ vanishes as Q approaches zero, and 2) the magnetic density of states vanishes approximately in proportion to ω as ω goes to zero.

We prepared a 50 g powder sample by solid-state reaction of stoichiometric amounts of Cr_2O_3 , Ga_2O_3 and SrCO_3 in air at 1350 °C. High-temperature magnetic-susceptibility data revealed a Cr^{3+} content corresponding to $p = 0.92(5)$. Neutron powder diffraction patterns were consistent with the previously reported structure [3] with 90(1)% Cr^{3+} occupancy in the kagomé ($12k$) planes and 89(3)% in the intervening triangular ($2a$) lattice planes [9]. The two-dimensional magnetic behavior of SCGO(p) is associated with this three-layer (111) slab of a pyrochlore lattice with in-plane lattice parameter $a = 5.80 \text{ \AA}$ [3], [9].

The neutron scattering spectrometer was the IRIS instrument at the ISIS pulsed spallation source [10]. Neutron flight times identify the incident energy, while backscattering Pyrolytic Graphite (PG) or Mica analyzers fix the final neutron energy at 1.82 meV and 0.832 meV, respectively. The respective energy resolutions are 7.5 μeV and 2.25 μeV , half-width at half-maximum (HWHM) while the momentum resolution is determined by the 3° angular acceptance of each detector. For comparison the classical neutron spin echo measurements on ordinary spin glasses have extended to time scales of order nanoseconds corresponding to an energy of 0.7 μeV [11]. Magnetic neutron scattering from a powder sample probes the spherically averaged scattering function [12]

$$S(Q, \omega) = \int \frac{d\Omega_{\hat{Q}}}{4\pi} \frac{1}{2} \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) |F(Q)|^2 \frac{(g\mu_B)^2}{2\pi\hbar} \cdot \int dt \exp[i\omega t] \frac{1}{N} \sum_{\mathbf{R}\mathbf{R}'} \langle S_{\mathbf{R}}^\alpha(t) S_{\mathbf{R}'}^\beta(0) \rangle \exp[-i\mathbf{Q} \cdot (\mathbf{R} - \mathbf{R}')], \quad (1)$$

where $F(Q)$ is the magnetic form factor of a single Cr ion [13]. Absolute values for $S(Q, \omega)$ and the related dynamic susceptibility, $\chi''(Q, \omega) = \pi S(Q, \omega)(1 - \exp[-\hbar\omega/k_B T])$ (fluctuation-dissipation theorem), were derived by scaling to nuclear Bragg intensities. This normalization procedure is accurate to within $\pm 20\%$. Throughout we normalize to the number of chromium

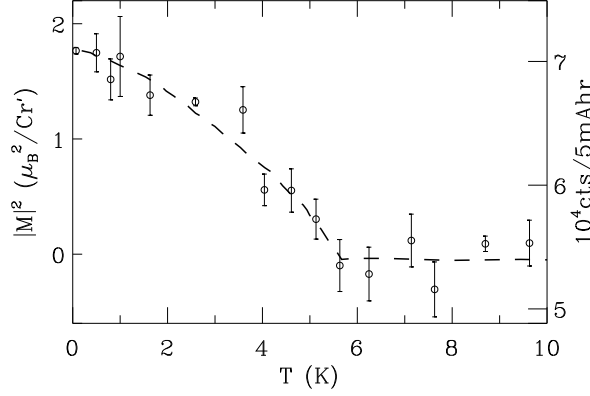


Fig. 1. – T -dependence of wave vector averaged elastic neutron scattering in SCGO($p = 0.92(5)$): $\int_{0.7 \text{ \AA}^{-1}}^{1.25 \text{ \AA}^{-1}} Q^2 dQ (\bar{S}(Q)/|F(Q)|^2) / \int_{0.7 \text{ \AA}^{-1}}^{1.25 \text{ \AA}^{-1}} Q^2 dQ$. The data was obtained using the Mica analyzer on IRIS. The corresponding energy resolution is 2.25 μeV HWHM. The dashed line is a guide to the eye.

atoms (Cr') in the pyrochlore slabs.

Figure 1 shows wave vector integrated elastic neutron scattering intensity as a function of temperature. The onset of elastic magnetic scattering for $T < 5$ K signals the development of magnetic correlations on a time scale, $\tau > \hbar/\Delta E = 0.3$ ns, set by the energy resolution of the instrument [14]. Anomalies in DC and low-frequency ($\nu = 1$ Hz) AC susceptibility measurements, on the other hand, establish that spin correlations which are static on a time scale of $1/2\pi\nu \approx 1$ s do not appear until $T = 3.4$ K [4]-[6]. The frequency dependence of the apparent freezing temperature which the comparison of these experiments implies is one of the defining characteristics of a spin glass [15].

Elastic neutron scattering yields direct microscopic information about the frozen spin configuration. Magnetic scattering associated with the frozen spin state at $T = 70$ mK was isolated from raw data by subtracting a high-temperature ($T = 20$ K) background. Figure 2a) shows the Q -integral of such difference data. The $\hbar\omega$ -dependence of the data appears to be resolution-limited so the experiment can establish only a lower limit for the characteristic life time, τ , of the frozen spin configuration. To determine this limit, we compare the data to the convolution of the measured resolution function with a generalized Lorentzian, $S(\omega) \propto (1 + (\omega\tau)^2)^{-\eta}$. From this analysis we conclude that $\tau > 7$ ns and $\eta > 0.8$ ⁽¹⁾.

Integrating the difference data over both Q and ω yields the following estimate of the average frozen moment $|M|^2 \approx 3 \int_{0.4 \text{ \AA}^{-1}}^{1.86 \text{ \AA}^{-1}} (\bar{S}(Q)/|F(Q)|^2) Q^2 dQ / \int_{0.4 \text{ \AA}^{-1}}^{1.86 \text{ \AA}^{-1}} Q^2 dQ = 3.6(6) \mu_B^2/\text{Cr}'$ ⁽²⁾. This quantity is substantially less than its counterpart in conventional antiferromagnets and ferromagnets built from Cr^{3+} ions where $|M|^2 = (gS\mu_B)^2 = 9\mu_B^2/\text{Cr}$ which attests to the tenuous nature of magnetic order in SCGO($p = 0.92(5)$).

The spatial correlations of the frozen spin state are examined in fig. 2b) which shows the Q -dependence of elastic magnetic scattering, $\bar{S}(Q)$, at $T = 70$ mK. For $0.4 < Q < 1.86 \text{ \AA}^{-1}$ we observe a single broad peak at a *finite* wave vector $Q = 1.5 \text{ \AA}^{-1}$. This indicates the presence of short-range antiferromagnetic correlations. The length scale associated with the HWHM (0.38 \AA^{-1}) of the peak is only $\xi_{\text{HWHM}} = 2.6 \text{ \AA}$, unusually small for a weakly diluted magnet. Even more surprising is that $\bar{S}(Q)$ appears to vanish as $Q \rightarrow 0$. A vanishing elastic forward-

⁽¹⁾ Exceeding these limits causes a statistically significant deviation of model from data.

⁽²⁾ This value is larger than the value quoted in fig. 1c) because the Q -integral taken there does not fully include the peak in $\bar{S}(Q)$.

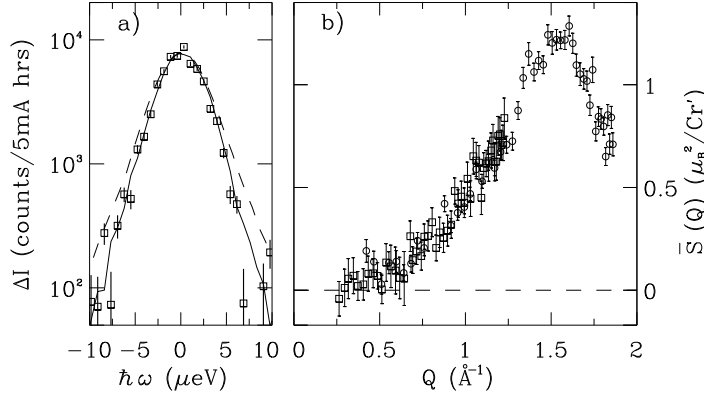


Fig. 2. – $\hbar\omega$ - and Q -dependence of near elastic scattering in SCGO($p = 0.92(5)$). *a*) compares the $\hbar\omega$ -dependence of wave vector integrated magnetic scattering at $T = 70$ mK to that of the measured instrumental resolution (solid line). The dashed line is the convolution of a $0.5 \mu\text{eV}$ HWHM Lorentzian with the instrumental resolution. *b*) shows the Q -dependence of the elastic magnetic scattering intensity, $\bar{S}(Q)$. Squares are for the Mica analyzer, circles for the PG analyzer. A high-temperature background (8.7 K for the squares, 20 K for the circles) was subtracted from the data in frames *a*) and *b*).

scattering cross-section is very significant, because it implies that there exists a decomposition of the frozen spin state into subgroups of spins such that each subgroup possesses net spin zero. Since $\bar{S}(Q)$ vanishes on a Q -scale of order the in-plane reciprocal lattice vector ($a^* = 1.25 \text{ \AA}^{-1}$) the zero-spin subgroups could be pairs, triangles or tetrahedra of nearest-neighbor Cr^{3+} ions. It is remarkable that “local antiferromagnetic constraints”, similar to those satisfied within the unit cells of long-range ordered antiferromagnets, are satisfied *without* long-range order in the frozen state of SCGO($p = 0.92(5)$). Shender *et al.* [16] have shown that the ground state of the weakly diluted classical kagomé antiferromagnet obeys a “rule of satisfied triangles”. Our data suggest that a frozen spin state consisting of satisfied triangles and tetrahedra may in fact be realized in SCGO($0.92(5)$) ⁽³⁾.

It is interesting to note that, even though the elastic magnetic scattering cross-section at $T = 70$ mK vanishes as $Q \rightarrow 0$, the homogeneous susceptibility $\chi'(Q = 0) = \int d\omega S(Q = 0, \omega)(1 - \exp[-\beta\hbar\omega])/\omega$ does not [4], [17]. Such behavior is also expected for long-range ordered isotropic antiferromagnets where $\int d\omega S(Q = 0, \omega) = 0$ at $T = 0$ [12], as well as for anisotropic antiferromagnets where a finite $Q = 0$ susceptibility is associated with a finite *inelastic* forward-scattering cross-section.

Low-energy excited states in the ordered phase of a magnet (if present) generally arise from slight perturbations of the order parameter. It therefore appears likely that the glass of zero-spin clusters in SCGO(p) has a different excitation spectrum than a conventional spin glass. To explore this possibility we measured the low-energy inelastic magnetic neutron scattering spectrum at various temperatures above and below the freezing transition. Figure 3 shows the outcome as a plot of the imaginary part of the local susceptibility, $\chi''(\omega) = \int Q^2 dQ \chi''(Q, \omega) / \int Q^2 dQ$ for three different temperatures. An energy-dependent background, determined by imposing the detailed balance constraint ($S(Q, -\omega) = \exp[-\beta\hbar\omega]S(Q, \omega)$) on scattering at four different temperatures, was subtracted from the raw data before deriving the absorptive part of the response function via the fluctuation dissipation theorem. Upon

⁽³⁾Note that samples with lower p have more elastic small-angle magnetic scattering as well as larger low- T bulk susceptibilities. Both results indicate that vacancies eventually produce “fragments” of the magnetic lattice whose moments do not cancel at low T .

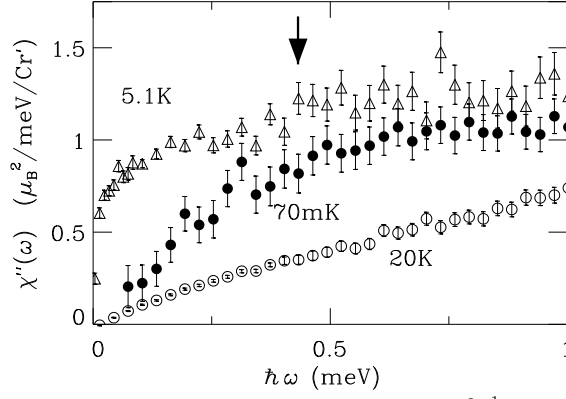


Fig. 3. – The imaginary part of the local susceptibility $\chi''(\omega) = \frac{\int_{0.64 \text{ \AA}^{-1}}^{1.84 \text{ \AA}^{-1}} Q^2 dQ \chi''(Q, \omega)}{\int_{0.64 \text{ \AA}^{-1}}^{1.84 \text{ \AA}^{-1}} Q^2 dQ}$ as derived from background-subtracted inelastic magnetic neutron scattering data. The arrow indicates the value of $k_B T$ where C/T is largest in our sample.

lowering the temperature from 20 K to 5 K, $\chi''(\omega)$ softens, in the sense of displaying a lower energy $\hbar\Gamma$ at which it crosses from approximately linear (in ω) to flat behavior. This is in accord with expectations for a conventional spin-glass transition which is characterized by a gradual divergence of the lowest time scale for magnetic fluctuations. What is unusual, however, is that low-frequency degrees of freedom are depleted in the frozen state where $\chi''(\omega) \propto \omega$ up to a characteristic energy scale $\hbar\Gamma = 0.5$ meV. Conventional spin glasses retain their characteristic slow dynamics even in the low- T limit as evidenced by their characteristic nearly ω -independent χ'' . Moreover the specific heat, $C(T)$, of such systems rises in proportion to T [18] implying a frequency-independent density of excited states. For SCGO($p = 0.92(5)$), however, $\chi''(\omega) \propto \omega$ for $\hbar\omega < 0.5$ meV and $C(T) \propto T^2$ for $k_B T < 0.5$ meV, both results which imply that the density of excited states, $\rho(\omega)$, for this frozen spin state rises in proportion to ω for $\hbar\omega < 0.5$ meV. Both specific heat [5] and inelastic neutron scattering [7] indicate that $\hbar\Gamma$ decreases with occupancy, p , of the magnetic lattice ⁽⁴⁾ and therefore it is likely that cooperative—as opposed to single-ion—effects are responsible for the unusual low-energy limit of $\rho(\omega)$.

It has been pointed out [5], [2] that the quadratic temperature dependence of specific heat in SCGO(p) might arise from the Goldstone mode of the frozen spin state for which Halperin and Saslow [19] derived a hydrodynamic theory. The latter theory predicts that at sufficiently low energies, $\rho(\omega) \propto \omega^{D-1}$. In principle the theory applies to any spin-glass but, as mentioned above, the thermomagnetic properties of conventional spin-glasses invariably give evidence for frequency-independent densities of states. It is generally agreed that this is because low-energy localized modes, which are not accounted for by the hydrodynamic theory, dominate the excitation spectrum of these systems in the experimentally accessible energy range. This is even true for numerical simulations of classical Heisenberg antiferromagnets on kagomé lattices [20]. The question is thus why this is *not* the case for SCGO($p = 0.92(5)$). There are several possible reasons including single ion and exchange anisotropies as well as quantum effects and the kagomé bi-layer nature of SCGO(p), all of which merit theoretical attention given our experimental results.

⁽⁴⁾For example in a $p = 0.79$ sample, the maximum in C/T vs. T occurs for $k_B T = 0.26$ meV [5] and $\chi''(\omega)$ is $\hbar\omega$ -independent for $0.2 \text{ meV} < \hbar\omega < 2 \text{ meV}$ [7], which indicates that $\hbar\Gamma \approx 0.2$ meV.

In summary, we have discovered that many aspects of the temperature-dependent spin correlations in SCGO($p = 0.92(5)$) are unprecedented for both spin-glasses and conventional magnets. In particular, as for the ordered state of spin-glasses but not ordinary magnets, there are no long-range two-spin correlations. At the same time, as for antiferromagnets but not for ordinary spin-glasses, the elastic scattering cross-section seems to vanish in the forward direction. Finally, there are two characteristic low-energy scales at low temperatures. The first is $\hbar/\tau < 0.1 \mu\text{eV}$ and corresponds to a spin autocorrelation time $\tau > 7 \text{ ns}$. The second is $\hbar\Gamma \approx 0.5 \text{ meV}$, which marks the onset of a plateau in the frequency-dependent local magnetic response, $\chi''(\omega)$. For $\hbar/\tau < \hbar\omega < \hbar\Gamma$, $\chi'' \propto \omega$ which is consistent with the quadratic T -dependence of the specific heat, but differs from what is ordinarily seen in spin glasses as well as from expectations for slightly disordered classical kagomé magnets [20]. That quantum effects [21] are important is obvious given that the frozen moment which persists on a time scale $\tau > 7 \text{ ns}$ is 40% below the maximum possible for $S = 3/2$ (Cr^{3+}) ions.

We thank P. COLEMAN, P. CHANDRA, and C. L. HENLEY for helpful discussions, and T. AMBROSE for technical assistance. NSF grants DMR-9302065, DMR-9453362, and DMR-9406115 supported work at JHU.

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